Oxidative alkylation of (η5-C5Me5)2TiR (R = Cl, Me, Et, CH=CH2, Ph, OMe, N=C(H)tBu) to (η5-C5Me5)2Ti(Me)R by group 12 organometallic compounds MMe2

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Oxidative alkylation of $(\eta^5\text{-}C_5Me_5)_2TiR$ (R = Cl, Me, Et, $CH{=}CH_2$, Ph, OMe, $N{=}C(H)^tBu$) to $(\eta^5\text{-}C_5Me_5)_2Ti(Me)R$ by group 12 organometallic compounds MMe_2

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Abstract

Oxidative alkylation of $Cp^★_2TiX$ ($Cp^★$: $\eta^5\text{-}C_5Me_5$; X = OMe, Cl, $N{=}C(H)^tBu$) and $Cp^★_2TiMe$ by $CdMe_2$ or $ZnMe_2$ gives diamagnetic $Cp^★_2Ti(Me)X$ and $Cp^★_2TiMe_2$ respectively, and cadmium or zinc. The reactions of $Cp^★_2TiR$ (R = Et, $CH{=}CH_2$, Ph) with MMe_2 (M = Cd, Zn) give statistical mixtures of $Cp^★_2Ti(Me)R$, $Cp^★_2TiMe_2$ and $Cp^★_2TiR_2$. Dimethylmercury does not react with $Cp^★_2TiX$.

Introduction

We previously described the preparation of $Cp^★_2Ti(R)Cl$ ($CP^★$: $\eta^5\text{-}C_5Me_5$; R = alkyl, aryl, H) by oxidative chlorination of $Cp^★_2TiR$ complexes with $PbCl_2$ [1]. Subsequent treatment of $Cp^★_2Ti(R)Cl$ with lithium, sodium or potassium reagents MR' gave (mixed) bis alkyl/aryl complexes $Cp^★_2Ti(R)R'$ [2]. However, in most cases the products were unstable at temperatures at which they were formed ($\approx$ -10 ° C). This considerably handicapped our attempts to study C-H activation in these tetravalent titanium hydrocarbyls. For this reason we tried to develop a new, low temperature, route to mixed $Cp^★_2Ti(R)R'$ derivatives. In view of the clean oxidation of $Cp^★_2TiR$ with $PbCl_2$, we decided to explore oxidative alkylation of $Cp^★_2TiR$ with group 12 dialkyl complexes MR'_2 (eq. 1).

$$Cp^★_2TiR + ½MR'_2 \rightarrow Cp^★_2Ti(R)R' + ½M \quad (1)$$

M = Zn, Cd, Hg; R' = Me, Et

The results are described below. Preliminary data on the oxidative alkylation of $Cp^★_2TiX$ (X = OMe, Cl) with $ZnMe_2$ have been published [3]. Recently, comparable oxidation reactions between Cp'_3SmNa and $AlH_3 \cdot THF$ were reported to yield $Cp'_2SmAlH_4 \cdot THF$ (Cp': $\eta^5\text{-}C_5H_4{}^tBu$), and that between $Cp^★_2Sm$ and Al_2Et_6 to give $Cp^★_2SmAlEt_4$ [4].

Experimental section

All operations were performed under an inert atmosphere by Schlenk, vacuum-line or glove box techniques. Solvents were distilled from Na/K alloy prior to use. $Cp^{\star}_2TiCl$ was synthesized by a published procedure [5a]. The compounds $Cp^{\star}_2TiR$ (R = Me, Et, C_2H_3, Ph) were prepared from $Cp^{\star}_2TiCl$ and Grignard reagents in diethyl ether [5b], $Cp^{\star}_2TiOMe$ from $Cp^{\star}_2TiMe$ and methanol, $Cp^{\star}_2TiN{=}C(H)^tBu$ from $Cp^{\star}_2TiEt$ and $^tBuC{\equiv}N$ [6]. Organocadmium compounds were prepared as described previously [7] from $CdCl_2$, and dimethylzinc was prepared as previously described [8]. $HgMe_2$ (Merck-Schuchardt) was used as received. IR spectra were recorded on a Pye Unicam SP3-300 or Bruker IFS-88 as Nujol mulls between KBr disks. NMR spectra were recorded in benzene-d_6 on Bruker WH-90 or Varian VXR-300 spectrometers. Chemical shifts are reported in ppm and referenced to residual protons in deuterated benzene ($\delta = 7.15$ ppm for ^{1}H NMR, $\delta = 127.96$ ppm for ^{13}C NMR). Elemental analyses were carried out at the Microanalytical Department of this University under the supervision of A.F. Hamminga. All data given are the average of at least two independent determinations.

*$Cp^{\star}_2Ti(Me)OMe$ (**1**)*

A solution of $Cp^{\star}_2TiOMe$ (402 mg, 1.15 mmol) in 10 mL of ether was cooled to -30 ° C and $CdMe_2$ (42 μL, 0.57 mmol) was added. A Cd mirror was immediately formed on the wall of the vessel. After 2 h the volatiles were removed under vacuum, and the yellow residue was extracted with ether. Crystallization at -80 ° C yielded 231 mg of yellow-orange **1** (0.63 mmol, 55%). ^{1}H NMR δ 1.79 (s, 30H, $Cp^{\star}$), 3.82 (s, 3H, OCH_3), 0.09 (s, 3H, CH_3). ^{13}C NMR δ 11.77 (q, C_5Me_5; J(CH) 126 Hz), 119.3 (s, C_5Me_5), 42.17 (q, Ti*Me*; J(CH) 124 Hz), 62.6 (q, O*Me*; J(CH) 139 Hz). IR: 2795 (m), 2720 (w), 1130 (vs), 1020 (m), 502 (s). Anal. Found: C, 72.05; H, 9.99; Ti, 13.13. $C_{22}H_{36}TiO$ calc.: C, 72.51; H, 9.96; Ti, 13.14%. A similar procedure was used for the reaction of $Cp^{\star}_2TiOMe$ with dimethylzinc (scale 0.34 mmol, room temperature, reaction time 48 h, yield 82% of **1**).

*$Cp^{\star}_2Ti(Me)Cl$ (**2**) and $Cp^{\star}_2Ti(Et)Cl$ (**3**)*

$Cp^{\star}_2TiCl$ (712 mg, 2.01 mmol) was suspended in 25 mL of pentane at -30 ° C and $CdMe_2$ (75 μL, 1.05 mmol) was added from a syringe. A red precipitate separated. Subsequently the mixture was allowed to warm to room temperature and after 2 h the volatiles were removed in vacuum and the orange-red residue was extracted with THF. The extract was kept at -80 ° C to give 458 mg (1.24 mmol, 62%) of red crystalline **2**. A similar procedure was followed for $Cp^{\star}_2Ti(Et)Cl$ (**3**), starting from 559 mg (1.61 mmol) of $Cp^{\star}_2TiCl$ and 83 μL (0.80 mmol) of $CdEt_2$. Yield: 312 mg **3** (0.82 mmol, 51 %). Both **2** and **3** were identified by comparison of their IR and NMR spectra with authentic samples [2]. Similar reactions of $ZnMe_2$ (scale 2.77 mmol) and $HgMe_2$ (scale 1.26 mmol) with $Cp^{\star}_2TiCl$ were carried out at room temperature in toluene.

*$Cp^{\star}_2Ti(Me)N{=}C(H)^tBu$ (**4**)*

$Cp^{\star}_2TiN{=}C(H)^tBu$ (763 mg, 1.90 mmol) was treated at -30°C with $CdMe_2$ (68 μL, 0.93 mmol) in 20 mL of ether. The mixture slowly turned yellow-orange. After 4 h stirring volatiles were removed under vacuum, and the residue extracted with

Table 1

Experimental conditions and yields in reaction of $CdMe_2$ with $Cp^{\star}_2TiR$

R	Solvent	T (° C)	Time (h)	Scale (mmol)	Yield (%)
Me	Et_2O	0	30	1.46	78
Ph	Et_2O	20	50	0.56	- [a]
C_2H_3	Pentane	-60	100	2.34	39
Et	Toluene	-60	100	1.06	- [a]
	THF	-60	100	1.11	- [a]

[a] The reaction products were not separately isolated; the composition was determined by ^{1}H NMR spectroscopy.

ether. The extract was kept at -80 ° C to give 575 mg (1.37 mmol, 73%) of crystalline **4** as a mixture of two isomers (ratio 6 : 1). ^{1}H NMR (ppm) major isomer: δ 1.70 (s, 30H, $Cp^{\star}$), 0.96 (s, 9H, ^{t}Bu), -0.27 (s, 3H, CH_3), 7.78 (s, 1H, C*H*N); minor isomer: δ 1.70 (s, 30H, $Cp^{\star}$), 0.97 (s, 9H, ^{t}Bu), -0.87 (s, 3H, CH_3), 7.05 (s, 1H, C*H*N). ^{13}C NMR (ppm) major isomer: δ 11.81 (q, C_5Me_5; *J*(CH) 126 Hz), 114.6 (s, C_5Me_5), 41.6 (s, *C*CMe_3), 27.3 (q, C(*C*H_3)$_3$; *J*(CH) 127 Hz), 163.9 (dm, *C*(H)N; *J*(CH) 163 Hz), 30.3 (q, Ti*C*H_3; *J*(CH) 123 Hz); minor isomer: δ 11.92 (q, C_5Me_5; *J*(CH) 125 Hz), 116.1 (s, C_5Me_5), 38.7 (s, *C*Me_3), 26.9 (q, C(*C*H_3)$_3$; *J*(CH) 127 Hz), 161.9 (dm, *C*(H)N; *J*(CH) 157 Hz), 39.7 (q, Ti*C*H_3; *J*(CH) 123 Hz). IR (cm^{-1}): 2745 (s), 2630 (m), 1765 (w), 1680 (vs), 1630 (w), 1360 (m), 1330 (w), 1250 (w), 1200 (s), 1170 (w), 1110 (w), 1065 (w), 1020 (m), 890 (w), 880 (w), 675 (s), 480 (m). Anal. Found: C, 74.27; H, 10.39; Ti 11.52. $C_{26}H_{43}TiN$ calc.: C, 74.79; H, 10.38; Ti, 11.47%.

Reactions of $CdMe_2$ with $Cp^{\star}_2TiR$ (R = alkyl, aryl) were performed similarly; for details see Table 1. Similar experimental procedures were used for the reactions of $Cp^{\star}_2TiR$ with $HgMe_2$ and $ZnMe_2$.

Results

Reaction of $Cp^{\star}_2TiX$ (X = Cl, OMe, N=C(H)^{t}Bu) with dimethylcadmium

It is known that Cp_2V (C;: η^5-C_5H_5) reacts with organocadmium compounds CdR_2 to form bis-alkyl complexes Cp_2VR_2 (R = Me, Et, CH_2Ph) [9]. Since oxidative alkylation is exactly the type of reaction we are interested in, an exploratory study was carried out with $CdMe_2$ as the oxidant. The anionic σ-bonded derivatives $Cp^{\star}_2TiOMe$, $Cp^{\star}_2TiCl$ and $Cp^{\star}_2TiN{=}C(H)^tBu$ were selected as substrate molecules, because the expected products $Cp^{\star}_2Ti(Me)X$ are stable and can be isolated and fully characterized at room temperature [2].

Reaction of $Cp^{\star}_2TiOMe$ and $CdMe_2$ at -30 ° C is immediate, and gives an orange solution of $Cp^{\star}_2Ti(Me)OMe$ (**1**) with deposition of Cd metal (eq. 2).

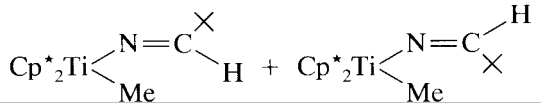
$$Cp^{\star}_2TiX + \tfrac{1}{2}CdMe_2 \rightarrow Cp^{\star}_2Ti(Me)X + \tfrac{1}{2}Cd \quad (X = OMe, \mathbf{1}; Cl, \mathbf{2}) \qquad (2)$$

$$Cp^{\star}_2TiCl + CdMe_2 \xrightarrow{\diagup\diagdown} Cp^{\star}_2TiMe + CdMeCl \qquad (3)$$

Similarly $Cp^{\star}_2TiCl$ was treated with $CdMe_2$ to give $Cp^{\star}_2Ti(Me)Cl$ (**2**) as the only organometallic product. The oxidative alkylation of $Cp^{\star}_2TiCl$ is a clean reaction.

There was no indication of reaction between $Cp^{\star}_2TiCl$ and $CdMe_2$ to give $Cp^{\star}_2TiMe$ and CdClMe (eq. 3). Also not observed were possible products such as $Cp^{\star}_2TiMe_2$ (*vide infra*) or $Cp^{\star}_2TiCl_2$, resulting from oxidation of the last two organotitanium compounds. From an analogous reaction between $CdEt_2$ and $Cp^{\star}_2TiCl$ the mono-ethyl derivative $Cp^{\star}_2Ti(Et)Cl$ (**3**) was isolated. The sterically more demanding azomethine complex $Cp^{\star}_2TiN{=}C(H)^tBu$ was smoothly oxidized by $CdMe_2$ to give the monomethylated product $Cp^{\star}_2Ti(Me)N{=}C(H)^tBu$ (**4**) (eq. 4). Compound **4** was isolated as a mixture of two isomers in a 6 to 1 ratio. * The asymmetry in **4** presumably originates from two inequivalent positions of the metal bonded methyl group relative to the azomethine proton.

$$Cp^{\star}_2TiN{=}C(H)^tBu + \tfrac{1}{2}CdMe_2 \xrightarrow{-\frac{1}{2}Cd}$$



(4)

Thus, oxidative alkylation of the 15-electron compounds $Cp^{\star}_2TiX$ (X = OMe, Cl, $N{=}C(H)^tBu$) with CdR_2 (R = Me, Et) to corresponding diamagnetic alkyl derivatives $Cp^{\star}_2Ti(R)X$ proceeds smoothly at low temperature. There is no evidence for side (substitution) or subsequent (disproportionation) reactions.

Reaction of $Cp^{\star}_2TiR$ (R = Me, Et, Ph, C_2H_3) with dimethylcadmium

The clean formation of **1**-**4** from the corresponding $Cp^{\star}_2TiX$ compounds looked very promising, so we decided to extend our investigations to alkyl and aryl derivatives $Cp^{\star}_2TiR$. Reaction of $Cp^{\star}_2TiMe$ with $CdMe_2$ at 0 ° C gave $Cp^{\star}_2TiMe_2$ in high yields, demonstrating that $Cp^{\star}_2TiR$ (R = alkyl) compounds are also readily oxidized (eq. 5).

$$Cp^{\star}_2TiMe + ½CdMe_2 \rightarrow \underset{(\mathbf{5})}{Cp^{\star}_2TiMe_2} + ½Cd \qquad (5)$$

However, reactions of other titanium alkyl derivatives $Cp^{\star}_2TiR$ with $CdMe_2$ were less straightforward. The vinyl derivative $Cp^{\star}_2TiC_2H_3$ reacted with $CdMe_2$ to $Cp^{\star}_2Ti(Me)C_2H_3$ (**6**), but the compound contained about 5% $Cp^{\star}_2TiMe_2$ *. The outcome was even worse for $Cp^{\star}_2TiEt$. $Cp^{\star}_2TiEt$ was treated with $CdMe_2$ at -60 ° C for 100 h during which a cadmium mirror was slowly formed. For analysis, the reaction mixture was filtered at low temperature (-30 ° C) and subsequently thermolyzed at room temperature. The originally yellow-orange solution turned green during this process (± 5 min). The ^1H NMR spectrum of the thermolysis mixture revealed the presence of two new compounds, $Cp^{\star}_2TiMe_2$ and $Cp^{\star}_2Ti(\eta^2\text{-}C_2H_4)$ [10], in a 1 to 3 ratio. The product ratio was independent of solvent (THF

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* This is indicated by the large shift difference between the both groups in the ^1H NMR spectrum (Me: -0.27 vs -0.87 ppm and N=C(H): 7.78 vs 7.05 ppm for the major and minor isomer, respectively, cf. ^{13}C NMR). In addition, in the IR spectrum of **4** there are two absorptions for the azomethide proton at $\nu(CH) = 2745$ cm^{-1} and 2630 cm^{-1}. for the major and minor isomer. respectively. Cf. J.E. Bercaw, D.L. Davies and P.T. Wolczanski, *Organometallics*, 5 (1986) 443.)

* Recrystallization from concentrated pentane extracts of the reaction mixture at 0 ° C allowed isolation of pure **6** in poor yield (39%).

or toluene). In a separate experiment, gas formed during thermolysis was collected with a Toepler pump, and shown to consist of a mixture of ethane and methane (1 to 2 ratio) to a total of 0.73 equiv. per titanium. This indicates the *in situ* formation of a statistical mixture of $Cp^{\star}_2TiMe_2$, $Cp^{\star}_2Ti(Et)Me$ and $Cp^{\star}_2TiEt_2$ (eq. 6). From other studies it is known that the last two compounds decompose to $Cp^{\star}_2Ti(\eta^2\text{-}C_2H_4)$ and methane or ethane, respectively [2]. Apparently, the alkyl ligands are readily exchanged at low temperature between tervalent titanium and cadmium (*vide infra*). The same mixture was formed by reaction of $Cp^{\star}_2TiMe$ and $CdEt_2$. This reaction is slower, and does not proceed at -60 °C but at -35 °C; slow formation of cadmium was again observed.

$$Cp^{\star}_2TiEt \xrightarrow[-Cd]{CdMe_2} \tfrac{1}{4}Cp^{\star}_2TiMe_2 + \tfrac{1}{2}Cp^{\star}_2Ti(Me)Et + \tfrac{1}{4}Cp^{\star}_2TiEt_2 \qquad (6)$$

$$\downarrow \text{-MeH} \qquad\qquad \downarrow \text{-EtH}$$

$$Cp^{\star}_2TiC_2H_4 \qquad Cp^{\star}_2TiC_2H_4$$

The phenyl derivative $Cp^{\star}_2TiPh$ did not react with $CdMe_2$ at low temperature (-35°C). At room temperature a slow reaction was observed: after 4 days' stirring some starting material was still present, together with a mixture of $Cp^{\star}_2TiMe_2$ [11], $Cp^{\star}_2Ti(Me)Ph$ [2] and $Cp^{\star}_2TiPh_2$ [11] (ratio $\approx 1:2:1$). Once again no clean oxidative alkylation was observed. Thus, alkyl and aryl derivatives of $Cp^{\star}_2TiR$ are oxidized to bis-alkyl (aryl/alkyl) complexes $Cp^{\star}_2Ti(R)R'$, but in contrast to anionic derivatives $Cp^{\star}_2TiX$, their reactions are accompanied by extensive disproportionations. Since isolation of pure compounds from the reaction mixture is practically impossible, the oxidative alkylation of $Cp^{\star}_2TiR$ with CdR'_2 is not a useful alternative to the treatment of $Cp^{\star}_2Ti(R)Cl$ with MR' reagents for preparation of mixed alkyl compounds $Cp^{\star}_2Ti(R)R'$. The usefulness of this reaction for the synthesis of $Cp^{\star}_2Ti(R)R'$ ($R \neq R'$) type compounds is therefore limited, but it certainly has potential for the synthesis of thermally labile $Cp^{\star}_2TiR_2$ complexes.

Since oxidative alkylation of $Cp^{\star}_2TiR$ did take place with $CdMe_2$, although without the selectivity needed for synthetic application, we turned our attention to other group 12 MMe_2 compounds.

Reaction of $Cp^{\star}_2TiCl$ and $Cp^{\star}_2TiR$ (R = Me, Et) with $HgMe_2$

No reaction was observed between $Cp^{\star}_2TiCl$ and $HgMe_2$, not even during 48 h at room temperature. Similarly when a mixture of $Cp^{\star}_2TiMe$ and $HgMe_2$ was stirred for 100 h at room temperature the $Cp^{\star}_2TiMe$ was almost completely recovered. In contrast, a rapid reaction was observed when $HgMe_2$ was mixed with $Cp^{\star}_2TiEt$ at 0 °C. The solution turned yellow within 15 minutes, and mercury separated. Analysis of the reaction mixture by ^1H NMR spectroscopy showed that, as when $CdMe_2$ was used, a mixture of $Cp^{\star}_2TiMe_2$ and $Cp^{\star}_2Ti(\eta^2\text{-}C_2H_4)$ (ratio 1/3) had been formed. The reason for the differences in reactivity between $Cp^{\star}_2TiMe$ and $Cp^{\star}_2TiEt$ towards $HgMe_2$ is not clear.

Reaction of $Cp^{\star}_2TiX$ (X = OMe, Cl) and $Cp^{\star}_2TiR$ (R = Me, Et) with $ZnMe_2$

Treatment of toluene solutions of $Cp^{\star}_2TiOMe$ and $Cp^{\star}_2TiCl$ with $ZnMe_2$ at room temperature slowly (ca. 24 h) gives quantitative yields of **1** and **2**, respectively. This is remarkable since dialkylzinc compounds are normally considered

substitution or reducing agents, rather than oxidants [12]. Reduction of **2** by zinc metal formed *in situ* was not observed; probably there is a kinetic reason for this, since zinc metal is known to reduce tetravalent titanium halides [13]. $ZnMe_2$ reacts more slowly than $CdMe_2$ with $Cp^{\star}_2TiOMe$ or $Cp^{\star}_2TiCl$. At 0 ° C no zinc precipitation was observed during 4 h in each case. As in the reactions with $CdMe_2$ no substitution or disproportionation reactions were observed with titanium species $Cp^{\star}_2TiX$ containing anionic substituents.

The reactions of $ZnMe_2$ with $Cp^{\star}_2TiR$ (R = Me, Et) closely resemble those of $CdMe_2$. $Cp^{\star}_2TiMe$ reacts quickly at room temperature with $ZnMe_2$ in toluene to give **5** in almost quantitative yield. In contrast to the slow reaction of $Cp^{\star}_2TiX$ with $ZnMe_2$, oxidation is complete within 0.5 hour at room temperature. Reaction of $Cp^{\star}_2TiEt$ with $ZnMe_2$ once again resembles that with other group 12 compounds MMe_2. Treatment of brown $Cp^{\star}_2TiEt$ with $ZnMe_2$ at -80°C gives a green solution, showing the characteristic color of $Cp^{\star}_2TiMe$, suggesting that ligand exchange takes place rather than oxidation (eq. 7). * Kept at -80 ° C no zinc precipitation was observed during 5 days. After 5 days at -35 ° C only a small amount of zinc had been formed. Apparently, ZnR'_2 reagents do not oxidize compounds $Cp^{\star}_2TiR$ at low temperature. At room temperature rapid precipitation of zinc was observed. Analysis of the reaction mixture with ^1H NMR showed that it again consisted of a mixture of $Cp^{\star}_2TiMe_2$ and $Cp^{\star}_2Ti(\eta^2\text{-}C_2H_4)$ (ratio 1 : 3).

$$Cp^{\star}_2TiEt + ZnMe_2 \rightarrow Cp^{\star}_2TiMe + ZnMeEt \qquad (7)$$

Apparently ligand exchange between MR'_2 (M = group 12 metal) and $Cp^{\star}_2TiR$ is faster than oxidative transfer of an alkyl group, making them unsuitable for the synthesis of mixed bisalkyl $Cp^{\star}_2Ti(R)R'$ compounds. Synthesis of $Cp^{\star}_2Ti(Me)X$ (X: anionic σ-bonded group) by oxidative alkylation certainly has useful synthetic potential [3].

Discussion and conclusions

Oxidative alkylation

Compounds $Cp^{\star}_2TiX$ (X = OMe, Cl, N=C(H)^{t}Bu) and $Cp^{\star}_2TiR$ (R = alkyl, aryl) are oxidized by zinc and cadmium MR'_2 compounds to $Cp^{\star}_2Ti(R')X$ and $Cp^{\star}_2Ti(R')R$. The cadmium compounds react more rapidly than the zinc complexes, and in general $Cp^{\star}_2TiR$ (R = alkyl) are more readily oxidized than $Cp^{\star}_2TiX$. Oxidative addition reactions of ZnR_2 were not previously known, but have now been shown to proceed like those of the corresponding cadmium compounds [12]. Mercury derivatives do not react with tervalent $Cp^{\star}_2TiX$ and $Cp^{\star}_2TiR$ compounds by oxidative alkyl transfer.

Mechanism of oxidative alkylation

The oxidative alkylations of Cp_2V [9] and $Cp^{\star}_2V$ [14] with $CdMe_2$ to give dialkyl derivatives Cp_2VR_2 and $Cp^{\star}_2VR_2$ respectively, were reported previously. The reaction was judged to proceed by a complex route, starting with insertion of carbenoid vanadocene into a Cd-C bond. Oxidative alkylation of $Cp^{\star}_2TiX$

* This was confirmed by oxidizing the cold reaction mixture with $PbCl_2$, to give some $Cp^{\star}_2Ti(Me)Cl$ (^1H NMR [1]).

($Cp^{\star}_2TiR$), which has one unpaired electron, cannot proceed in this way and a low energy concerted process is more likely. Fast radical (and non-radical) self-exchange of alkyl groups between group 12 dialkyls, e.g. $CdMe_2$, has been reported [15,16], indicating that despite fairly high dissociation energies for the first homolysis D_1 (> 45 kcal/mol [17]), low activation energy processes are feasible through multicenter transition states. The rapid, non-oxidative ligand exchange indicates that $ZnMe_2$ (and also Cd) interact with $Cp^{\star}_2TiR$ compounds. Although no mechanistic studies were carried out, it is reasonable to assume that in this interaction a radical pathway becomes kinetically accessible. It can also be predicted that oxidative alkylation is likely to be accompanied by disproportionation.

Thermodynamic consequences

The observed oxidative alkylation of $Cp^{\star}_2TiX$ and $Cp^{\star}_2TiR$ by $ZnMe_2$ also has some thermodynamic implications. The mean M-C bond dissociation energy of 44 kcal/mol in $ZnMe_2$ sets a lower limit for the Ti-C bond dissociation energy of 44 kcal/mol. This is consistent with data for reaction solution calorimetric studies by Dias (D(Ti-Me) = 67.2 kcal/mol in $Cp^{\star}_2TiMe_2$) [18]. Since the determination of carbon-metal bond dissociation energies is not always experimentally simple, this type of oxidation reaction could (at least) be helpful for estimating lower limits for dissociation energies.

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